Fate of Arsenicals in Different Environmental Substrates ·

by E. A. Woolson*

The current knowledge of arsenic (As) transformations in the environment, as well as some gaps in this knowledge, are reviewed. These transformations involve As chemical and biochemical transformations in air, waters, sediments, and soils. Arsenic moves in a dispersive manner through air and water and is in physical and chemical equilibrium in many substrates. It is oxidized, reduced, methylated, volatilized, incorporated into biotic tissues, excreted, adsorbed, and desorbed. Oceanic sediments become the eventual sink for As.

The rates of As movement and transformation vary with environmental conditions. Besides inorganic As, various methylated arsenicals are found naturally at environmentally sensitive equilibrium concentrations, which are probably maintained biotically.

An As-transformation model has been constructed from rate constants derived from field observations. The environmental factors affecting these rate constants are discussed.

Arsenic in Soil

Arsenic (As) is found in all environmental substrates and has recently been shown as an essential element for rats (1). Only at high exposure levels, usually industrial, has it become a human and environmental problem. Normally, As used commercially as a pesticide and a nonpoint source is not present in high enough concentrations to present serious environmental problems. However when the soil and/or environmental conditions cannot detoxify the As levels applied, soil As toxicity becomes a problem. Since most environmental contamination from point sources (i.e., smelters and coal burning electric plants) will be reduced, as stricter air pollution controls are required, this paper will be limited generally, to fate and transformations that occur agriculturally at relatively low As concentrations. These same processes, however, may also occur from point sources.

Arsenic, as a labile element, is subject to several processes in the soil. Under various conditions, it is oxidized, reduced, methylated, volatized, adsorbed, and desorbed.

Besides smelters and coal-burning electric plants, As compounds contaminate the soil in the form of

pesticides from the burning of cotton wastes, from natural weathering processes, and in runoff from mining operations.

Of all the As sources reaching the soil, As pesticides are the most widely distributed geographically. Arsenic acid (H_3AsO_4) is applied to cotton for leaf desiccation or to vegetation as a general weed killer. Lead and calcium arsenates are insecticides used to kill leaf chewing insects. The organic arsenicals, methanearsonic acid (MAA; sodium salts MSMA and DSMA) and cacodylic acid (dimethylarsinic acid, CA) are selective and general postemergence herbicides, respectively. Arsenates are the oxidized degradation products from the organoarsenicals also, although under moderately reduced conditions (2), arsenite may be formed both biotically and abiotically. All other transformations are biotic. The arsenicals are adsorbed to amorphous iron and aluminum oxides, which coat the clay particles (3) or react with cations in the soil solution. Arsenate can also be associated with geothite particles, $HFeO_2$, (4).

The adsorption of arsenate to clay depends on soil pH, texture, Fe, Al, organic matter, and the elapsed time after exposure. As the soil's clay content increases, the As amount adsorbed increases (5). Equilibrium conditions are reached slowly with the soluble arsenate decreasing continually (6) and the Fe and Al forms stabilizing. Some As is always

*Pesticide Degradation Laboratory, AEQI, U. S. Department of Agriculture. Beltsville, Maryland 20705.

present in the soil solution and is probably the form available for biotransformation and plant uptake. Soluble As is also subject to leaching, especially in a sandy soil (5).

Arsenate can be reduced and methylated in soil (7), but this process is slow: from 10 ppm applied only 1 to 2% was volatilized as dimethylarsine [DMA; $(CH_3)_2AsH$] in 160 days.

The organoarsenical herbicides react like arsenate in soil—they are adsorbed on clay surfaces by Fe and Al oxides, leached from sandy soils, and subject to metabolism (8). Arsanilic acid, a feed additive, is also fixed to clay surfaces and metabolized to arsenate (9). The degree of fixation decreases as methyl groups are added to the As atom (6, 10).

Arsenic in Water

Inorganic As can exist in several oxidation states and forms in water (11), depending on the pH and Eh of the water. In a stratified lake, many reactions occur (Fig. 1). The adsorption of arsenate by Fe and Al oxides in sediments and formation of As_2S_3 removes As from solution and prevents large As concentrations from being present in water.
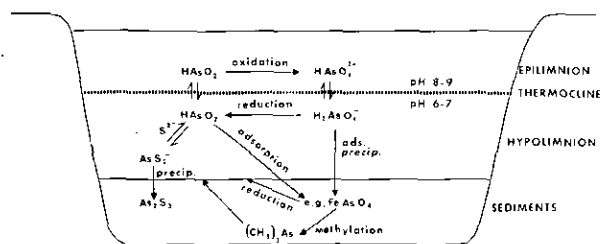

FIGURE 1. Arsenic reactions in a stratified lake [taken from Ferguson and Gavis (11)].

Concentrations in Lake Michigan water (0.5–2.3 $\mu g/l$.) are generally much less than that in its sediments (7.2–28.8 mg/kg) (12, 13). Sediments quickly remove As from streams containing high As inputs, with a resultant increase in the As concentration of sediment. The adsorption is probably associated with Fe and Al oxides, as in soils. Movement of As within the stream can be the result of dissolved load or the movement of suspended sediment (14). Formation of small amounts of volatile organo-arsines also remove As from streams.

Ferguson and Gavis (11), who estimated that the total As moved to the oceans was 30 × 10⁶ kg/yr, saw no imminent increase in oceans levels from this input.

Arsenate is reduced to arsenite, apparently by bacteria in the marine environment. Observed ratios of arsenate to total As were about 0.8 (15,

16). Thermodynamic calculations indicated a 10^{26} :1 ratio of $As(^{+5})$:$As(^{+3})$ in oxygenated seawater at pH 8.16 (17).

Arsenate in both fresh and salt water is metabolized to methylated compounds. Mono-, di-, and trimethylarsenicals have been isolated from both sources (16). The relative amounts of As^{+3}, As^{+5}, MAA, and CA vary, but generally As^{+5} and CA predominate. Arsenic is methylated by bacteria and fungi in water and/or sediments. Reactions of the organoarsenicals in water, however, have not been investigated. Organisms accumulate organoarsenicals, regardless of the form (18–20). Some metabolism does occur, but it may be within the host organism. Biomagnification through the food chain, however, does not occur with the arsenicals (21). Lower members of the aquatic food chain contain the highest residues.

Natural Concentrations of Total Arsenic

Most residue values have been reported only as total As. In soil, As levels normally range from 1 to 40 ppm total As (22). These values were derived from weathered parent rock material and As may have been present as arsenate or arseno-sulfides. The U. S. National Soils Monitoring Program reported As values for 12 states in the Corn Belt as ranging from 0.10 to 22.75 ppm; and averaging 2.74 (23). Residues from cropland in 43 states ranged from 0.25 to 54.17 ppm As and averaged 6.43 ppm for 1969 samples (24). However, some of these samples received As applications. In several states soil residues in untreated cropland were compared with that in cities. Five of six cities had higher soil residues (9.9 ppm) than did soils from cropland (5.2 ppm). This may be attributed to As deposition from industrial or combustion sources (24), rather than to differences in use of various arsenical pesticides.

Arsenic residues in water are generally low. Durum, Hem, and Heidel (25), who examined U. S. surface waters, reported that 79% of 727 samples examined had less than 10 μg As/l., the recommended drinking water standard; only 2% contained more than the mandatory upper limit for drinking water of 50$\mu g/l$. By the time water is treated and distributed to the general populace, only five of 2595 systems (0.2%) exceeded the mandatory limit for As in drinking water, while five others exceeded the recommended limit (26). Concentrations of As in seawater generally range from 0.15 to 6$\mu g/l$. with an average of about 2 $\mu g/l$. Concentrations in seawater tend to be higher at the river

outflows because of dissolved As and sediment load (11).

Sediments, even in areas with some industrial input, remain at a relatively low level. Lake Michigan contained 11 ppm As in the sediment with an estimated 145,000 kg As/yr input (12). Residues in the Puget Sound sediments, where smelter contamination was not a factor, varied from 3.2 to 15 ppm As (27), while those contaminated contained up to 10,000 ppm As, the content in slag. These background concentrations (3–11 ppm As) resemble those reported for deep sea sediments (28) and are positively correlated with organic matter (29), clay, extractable Fe and Al compounds (27), and decreasing particle size (13, 28).

Natural Concentrations of Organoarsenicals

Measurements of natural concentrations of organoarsenical compounds have suffered from lack of specific methodology necessary for speciation. Recent developments in technology have allowed speciation in a limited number of studies. Methylated arsenicals are formed naturally by various fungi (30), bacteria (31), molds (32), animals (33, 34), and aquatic organisms (16). Concentrations of the transformed arsenical are dose related in those instances where As was added to the system. Braman (16) reported natural environmental concentrations of arsenical compounds in fresh and salt water that ranged from 0.02 to 0.22 ppb for MAA, 0.15 to 1.00 ppb for CA, and 0.14 ppb for a trimethylarsenical with human urine containing 1.8 ppb MAA and 15 ppb CA. Aquatic weeds contained 10 ppb MAA and 64 to 185 ppb CA, while shrimp contained 72 ppb CA. No reports were found that described the natural levels of the organoarsenicals in the soil environment. However, a trimethyl compound was formed in a laboratory experiment (7). We might expect intuitively that low concentrations of alkylarsenicals are found under some soil conditions. We do not know if the organoarsenicals are photodegraded in water, air, or soil surfaces.

Dimethylarsine and trimethylarsine [TMA; $(CH_3)_3As$] were detected in air as a gas or adsorbed onto filterable particles. Outdoor levels were less than 1 ng/m³ and averaged 0.09 ng/m³ DMA and 0.08 ng/m³ TMA. Indoor home levels were higher, averaging 0.10 and 0.25 ng/m³, respectively. Little DMA was found as a gas in greenhouses, but TMA averaged 0.21 ng/m³. On filterable particles, greenhouse samples ranged to 27 ng/m³ ($x = 8.5$) TMA, but those from home and outdoor environments remained low (<0.5 ng/m³) (35).

Transport Cycle

Cycling of As in the environment is dominated by adsorption and desorption to soils and sediments. Significant As losses from the dissolved state are due to adsorption within hours in laboratory solutions (2, 6). Sediment movement can also account for large As losses from a watershed. With a polluted watershed, large amounts of As (probably from arsanilic acid wastes) were transported in the suspended state during high stream flow (14). At low flow rates, little sediment transport occurred while the water contained 15 to 59 µg/l, with a total dissolved As load of 1.8 to 3.5 kg/day. Only 0.2–0.3 kg/day was transported on suspended sediment under the same conditions. During flooding, large amounts of contaminated sediments will be moved. Nevertheless, much of the As moved to the oceans is in the dissolved state (30×10^6 kg/yr) (11).

At Tacoma, Washington, a smelter discharges large amounts of As_2O_3 into the air, and liquid effluent and slag into Puget Sound, where it is distributed by both wind and water. Wind movement accounts for high residues in soils and sediments on Vashon Island, because water flows away from and air moves toward the island. Sediments near the Tacoma smelter contain high levels of As (up to 10,000 ppm As). Surface seawater samples taken next to the smelter, contained a maximum 1200 ppb As. The concentration decreased very rapidly with distance to about 4 ppb within 1 mile from the smelter (36). Although the slag dumped into Puget Sound contained 1% As, this material is chemically and physically very stable in seawater and does not move from the site of deposition.

Yearly mass balance was calculated for the Puget Sound area. The inputs considered were sea and river water, precipitation, smelter effluent, Seattle sewage, and a drydock operation. Total inputs were estimated at $7.3 \pm 0.7 \times 10^8$ g As/yr, with 5.8×10^8 from seawater through Admiralty Inlet. The As content, flowing out of the sound in surface waters, indicated that $6.3 \pm 0.6 \times 10^8$ g As/yr were removed. The difference, $1.0 \pm 0.9 \times 10^8$ g As/yr, is that removed in the sediments. However, sedimentation is much less-important (14% of As input in this case) as a sink for As than that discharged through the Strait of Juan de Fuca (27).

Contamination of air from smelter stack emissions or from the burning of coal results in elevated As levels in the surrounding environment. Arsenic is returned to soil through either direct fallout as particulate matter or in precipitation. At the Tacoma smelter, an estimated 2×10^8 g As/yr are emitted in the stack gas (36). Total airborne losses, as As_2O_3, from the smelting of Cu ores was esti-

mated at 48 × 10⁸ g As/yr nationwide. Coal burning emits 6.5 × 10⁸ g As/yr into urban air (37). As a result, large cities have higher As levels in air than do small cities or rural areas (38). New York City air contained 30 μg/m³, with rural areas having less than 10 μg/m³. The As in air reaches the soil in rain or dust, where it is adsorbed and effectively removed from the transport cycle. This results in an elevated soil residue (24). Improvements in air pollution control should decrease As air concentrations and the amount reaching the soil.

Studies of the alkylarsenicals have indicated that biotransformations do occur; however, the transport mechanisms are less clear. Alkylarsines are formed in soil (7) and possibly sediments (16), and in sewage sludge (30). Thus transport occurs in two media, air and water.

Transport of alkylarsines in air may involve only the gaseous phase or perhaps a gaseous/particulate phase. The identity of alkylarsines adsorbed to particulates is unknown. They may be the oxidized form, MAA, CA, or TMA oxide, while that in the gaseous form is the alkylarsine. However, the extent of transport of the alkylarsines in air is unknown.

Also, transport of alkylarsenicals in waters is unknown. Fresh and salt waters have been shown to contain MAA and CA at low levels (16). Aquatic organisms can accumulate the alkylarsenicals to some extent (18–21). The lower food chain organisms contained the higher As residues. Metabolism to other compounds within fish may also occur (39–41). With the organo-arsenicals, movement probably occurs both through physical transport and through uptake by aquatic organisms.

Thus, the data indicate the fluvial transport of As is appreciable in a dissipative fashion downstream from point sources and that the bottom sediment of natural aquatic systems functions as a temporary reservoir in the dispersive transport of As. Oceanic sediments are the ultimate sink for As residues.
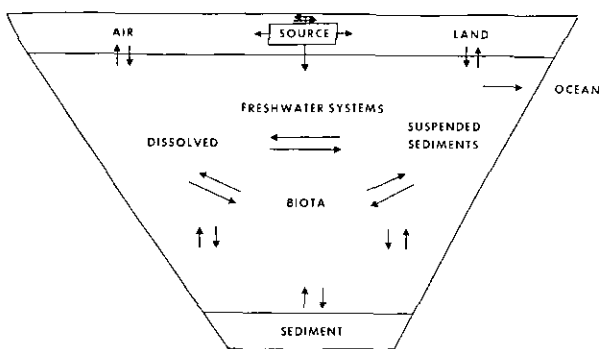

FIGURE 2. General flow processes of arsenic in the ecosystem.

Due to complex multimedia (sediment/soil–water–biota–air) exchange of As in the transport cycle and the natural differences between air, soil, and water systems, it is difficult to quantitate the degree of transport. We do know that As is sorbed by biota and sediments/soils, and is maintained at low concentrations in water and air. These processes of interchange are depicted in Figure 2. However, beyond intuitive reasoning, we know little of the rates of resuspension, desorption, and volatilization and the collective effects of environmental parameters controlling those rates.

Arsenic Transformations

Alkylarsines have been known environmentally, since Challenger et al. (42) identified "Gosio" gas as TMA. Gosio gas was generated by molds growing on wallpaper paste containing an As pigment. Various fungi, molds, and microorganisms can metabolize arsenate, arsenite, MSMA, and cacodylic acid to volatile arsenicals (10, 30, 31, 43–47). Usually DMA or TMA are the forms identified. Both have a "garlic" odor and sometimes appear in the air simultaneously above treated areas (16). Metabolism in soil seems to proceed through cacodylic acid to TMA oxide as evidenced by the work of Braman (16) and Woolson (7). After treating grass with CA, an initial high level of DMA in air decreased, while the level of TMA increased. The greater the degree of methylation of the As atom, the more rapid is the soil generation of alkylarsines (7).

In methylation studies, McBride and Wolfe (31) demonstrated that Methanobacterium strain M.o.H. reduced and methylated arsenate under anaerobic conditions to DMA. A methyl donor, methylcobolamin, was necessary. Cox and Alexander (30) isolated from sewage three fungi that produced TMA from either organic or inorgnic As sources. Lakso and Peoples (33) found both inorganic and methylated As in urine when cows or dogs were fed sodium arsenate or potassium arsenite. Urine levels for both forms (methylated and nonmethylated) increased during feeding with the organic forms predominant. The excretion half-life rate was about 1.5 days. Braman and Foreback (48) also found several forms of As in human urine. The average concentration (in ppb) and percent detected were: arsenite, 1.9 and 8; arsenate, 3.9 and 17; MAA, 1.8 and 8; CA, 15.0 and 66. Total residues averaged 22.5 ppb As. They concluded that CA is a major and ubiquitous form of As in the environment, particularly in biological systems. Although MAA was found, it was generally present in smaller

concentrations than CA, a probable consequence of its being only an intermediate in the As methylation sequence.

The environmental chemistry of As, as summarized by Braman (16), is given in Figure 3. Environmentally, neither arsine nor methylarsine has been detected in air. DMA and TMA are the volatile compounds that have been isolated and identified.

FIGURE 3. Conversion pathway for biotic metabolism of arsenic.
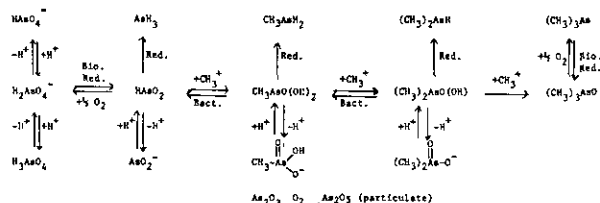
A very limited number of studies have examined the demethylation reactions of the organoarsenicals. Von Endt et al. (49) studied MSMA degradation in soil and found up to 10% of ^{14}C-MSMA was degraded to 60 days to $^{14}CO_2$ and arsenate (no arsenite was detected). Woolson and Kearney (10) detected arsenate in CA-treated aerobic soil. They found 41% was formed in 24 weeks from a 100 ppm treatment. No arsenate was detected under anaerobic conditions. ^{14}C-Cacodylic acid was degraded in a model ecosystem study (19) to arsenate, arsenite, and $^{14}CO_2$. In two of the three systems tested that contained soil, arsenate was the predominant form after 59 days. Total As was lost from the systems, presumably as an alkylarsine.

In the examination of arsenical feed additives (arsanilic acid; aminobenzenearsonic acid), Woolson (9) detected arsenate after 2 weeks under both aerobic and anaerobic soil conditions. Degradation to arsenate was fastest under anaerobic conditions. Little arsanilic acid (<10%) could be detected after 32 weeks incubation with most treatments. One soil lost total As.

Transformation Cycle

Figure 4 illustrates the postulated distribution, forms, and transformation of As in the environment. The As-transformation cycle is intimately involved with the transport cycle. Some of the stepwise transformation processes have been verified by the above-mentioned studies. Arsenicals in soils and sediments are in equilibrium with the surrounding environment, as well as with each other. The effect of many factors on this equilibrium is unknown: e.g., the As load required to upset this equilibrium; the carrying capacity of the various

systems (soil, water, sediment, biota); the rates of transfer between chemical entities within and between the various systems; and the identity of the As actually present in environmental components.

FIGURE 4. Cyclical nature of arsenic metabolism in different environmental compartments.

In addition, the role of the insoluble As compounds (Fe-, Al-, etc.) in soils and sediments in governing the biologic transformations and their rates is unknown. Intuitively, the arsenical might be expected to resist transformation, unless it were in solution (as shown in Fig. 5), where microorganisms can act upon the molecule. However, this perhaps is not the case. The nature of the TMA analog bound to soil is also unknown.

A second form of an As cycle (Fig. 6) shows the As fluxes within an agroecosystem. Here, soil represents the main As sink. Sandberg and Allen (50) calculated that in an agroecosystem 0.046–0.096 %/day (17–35 %/year) would be lost from the soil, when all inputs and losses are considered. Total losses by all processes, when CA is applied, ranged from 0.052 to 0.101 %/day, while the values for MSMA ranged from 0.055 to 0.070 %/day. At the maximum recommended application rates, total residues from CA would increase at the rate of 2.6–3.3 ppm/ha/yr, while residues from MSMA would increase at 1.5 to 1.9 ppm As/ha/yr. Losses to the air would be primarily as alkylarsines, although loss through dust is possible.
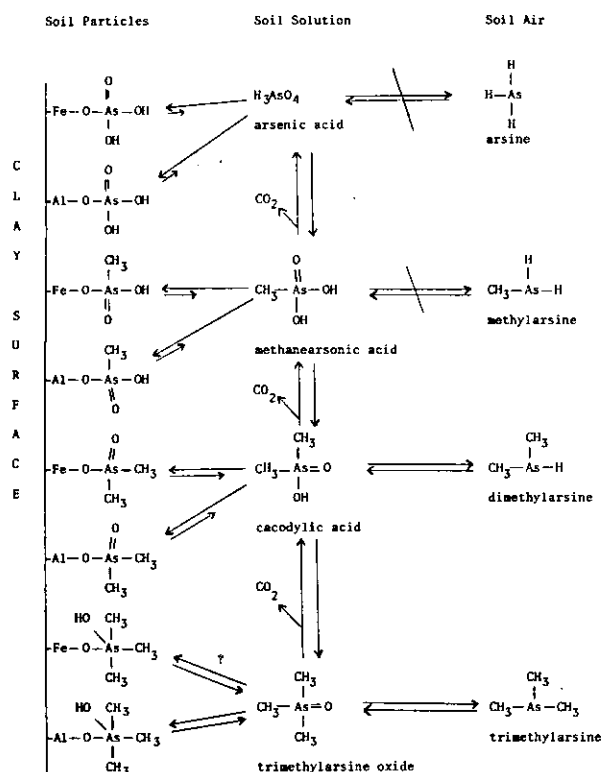
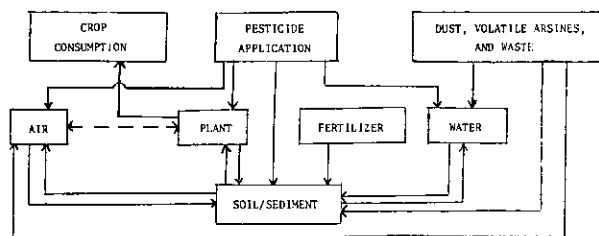FIGURE 5. Dissolution and reactions of arsenicals within the soil environment.

FIGURE 6. Fluxes of total arsenic in an agroecosystem [adapted from Sandberg and Allen (50)].

Rates of Transformation

Because of extreme difficulties in monitoring natural environmental systems and the lack of methodology (until recently) to distinguish between As compounds, no work has been reported on transformation rates per se under natural conditions. In a few instances, however, transfer rates can be inferred and calculated from previous experiments.

Two reactions can occur with any As compound: oxidative metabolism and reductive methylation with subsequent volatilization of the derived alkylarsine. The reactions and their rates will vary depending on environmental conditions. Data from several researchers were used to calculate that transformed or lost (in %/day) in various substrates (Table 1). The two types of studies represented included laboratory experiments designed to isolate and identify the volatile As compounds and field experiments where the As loss was measured over time. The As loss in these field studies, however, was not limited only to volatilization by alkylarsines, but included leaching, wind-borne dust, runoff, and crop removal.

Losses from field studies where arsenite was applied ranged from 0.010 to 0.124 %/day of the total As present. The average loss was computed at 0.030 %/day. This agrees with the laboratory experimental range reported by Woolson (7) for arsenate-treated soil. The calcium arsenate loss reported by Epps and Sturgis (45) is higher than the other values reported.

Field studies with MAA averaged 0.032 %/day loss for three experiments, whereas, losses in the laboratory experiment (7) were about twice as large. Based on two studies in different parts of the country, CA loss averaged 0.034 %/day. Again, values from the laboratory study were higher.
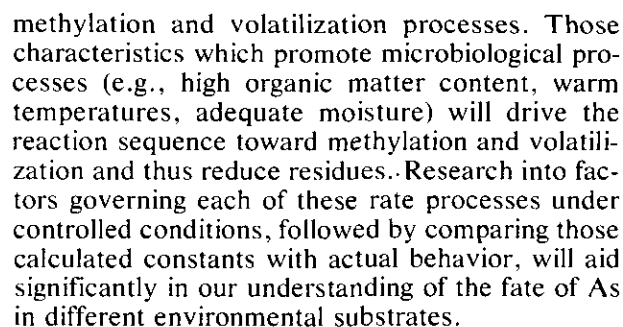
The loss rates of MAA and CA were similar, because oxidative metabolism is quicker and after an initial period, most of the As (regardless of the starting form) is likely to be at equilibrium within any particular soil. Intuitively, the concentration at this equilibrium may vary depending on soil characteristics (pH, Fe, Al, etc.), the organic matter content, rainfall, temperature, and soil microbial population. This may explain by some soils apparently have not lost very much As after lead arsenate application, while the As content in others seemed to decrease substantially (55).

In the field studies reviewed and tabulated in Table 1, the half-life for arsenate in soil was calculated as 6.0 yr, MAA as 5.6 yr, and CA as 5.2 yr.

The loss rates increase slightly with the increased methylation of the compound, which seems reasonable since fewer methylation steps are needed in MAA and CA to reach the DMA or TMA stage where reduction and volatilization can occur. Volatilization from aquatic systems was faster than from soil, although the evolved gases have not been isolated or identified. Loss was measured as total As from the system.

The necessary experiments to verify the rates of conversion and the identity of the transformed As compounds have not yet been performed.

The transformation As in the environment consists of a series of oxidations, reductions, methylations, and volatilizations and can be depicted as in Eq. (1):

$$AsO_1{}^{-3} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} AsO_3{}^{-3} \underset{K_4}{\overset{K_3}{\rightleftharpoons}} CH_3AsO_3{}^{-2} \underset{K_6}{\overset{K_5}{\rightleftharpoons}} (CH_3)_2AsO_2{}^{-1} \underset{K_8}{\overset{K_7}{\rightleftharpoons}} (CH_3)_3AsO$$

$$K_{10} \updownarrow K_9 \qquad\qquad K_{12} \updownarrow K_{11}$$

$$(CH_3)_2AsH \uparrow \qquad (CH_3)_3As \uparrow$$

$$(1)$$

The arsenicals present in water, sediment, or soil will be at equilibrium concentrations, unless one specific form is added. The nature of this equilibrium is unknown at present. Some soil and environmental characteristics will likely enhance the methylation and volatilization processes. Those characteristics which promote microbiological processes (e.g., high organic matter content, warm temperatures, adequate moisture) will drive the reaction sequence toward methylation and volatilization and thus reduce residues. Research into factors governing each of these rate processes under controlled conditions, followed by comparing those calculated constants with actual behavior, will aid significantly in our understanding of the fate of As in different environmental substrates.

Table 1. Fate of arsenicals in different substrates.

Substrate	Oxidative metabolism $(AsO_1{}^{-3})$, %/day		Volatilization* (reductive metabolism) (alkylarsines), %/day[a]	Reference
Soil	?[b]	$AsO_3{}^{-3}$	0.020–0.027	(51)
			0.023–0.067	(46)
			0.010–0.028	(52)
			0.035–0.124; $\bar{x}=0.035$	c
	—	$AsO_1{}^{-3}$	0.006-0.154	(7)
			(DMA, TMA)[d]	(46)
	—	$Ca_3(AsO_1)_2$	0.386	(49)
	0.081–0.476	MAA		(7)
			0.078 (DMA, TMA)	(53)
			0.038	c
			0.023–0.115; $\bar{x}=0.034$	(54)
			0.018–0.031	
		CA		
	0.244		—	(10)
			0.112–0.363 (DMA, TMA)	(7)
			0.033	(53)
			0.009–0.183; $x=0.034$	c
	0.046–0.086	Arsanilic Acid	0.0–0.163	(9)
Grass/soil	?	$AsO_3{}^{-3}$	<0.001 (DMA, TMA)	(16)
	?	MAA	0.014 (TMA)	(16)
	?	CA	0.026 (DMA, TMA)	(16)
Aquatic ecosystem	?	$AsO_3{}^{-3}$	?	
	—	$AsO_1{}^{-3}$	?	
	?	MAA	?	
	0.067–0.404	CA	0.084-0.814	(19)
				e
Fungi culture	?	$AsO_3{}^{-3}$	0.0–0.009	(30)
	—	$AsO_1{}^{-3}$	0.0–0.005 (TMA)	(30)
	0.272	MAA	0.0–2.960 (TMA)	(49)
				(30)
Bacteria culture	1.818	MAA	?	(49)
Actinomycete culture	0.818-1.182	MAA	?	(49)

[a]Based on loss of total arsenic in the soil; includes arsenic lost by any mechanism.

[b]? = not known.

[c]Unpublished data, E. A. Woolson, 1976.

[d]DMA = dimethylarsine; TMA = trimethylarsine; underlined species is predominant.

REFERENCES

1. Neilsen, F. H. Evidence of a possible requirement for arsenic in the rat. Fed. Amer. Soc. Exp. Biol. 34: 923 (1975).
2. Deuel, L. E., and Swoboda, A.R. Arsenic solubility in a reduced environment. Soil Sci. Soc. Amer. 36: 276 (1972).
3. Jacobs, L. W., Syers, J. K., Keeney, D. R. Arsenic sorption by soils. Soil Sci. Soc. Amer. Proc. 34: 750 (1970).
4. Fordham, A. W., and Norrish, K. Direct measurement of the composition of soil components which retain added arsenate. Austral. J. Soil Res. 12: 165 (1974).
5. Walsh, L. M., and Keeney, D. R. Behavior and phytotoxic-

ity of inorganic arsenicals in soils. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

6. Woolson, E. A., Axley, J. H., and Kearney, P. C. The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorus. Soil Sci. Soc. Amer. Proc. 37: 254 (1973).

7. Woolson, E. A. Generation of dimethylarsine from soil. Paper presented at 16th Meeting, Weed Science Society of America. 1976, paper No. 218.

8. Hiltbold, A. E. Behavior of organoarsenicals in plants and soils. In: Arsenical Pesticides (ACS Symposium Series 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

9. Woolson, E. A. The persistence and chemical distribution of arsanilic acid in three soils. J. Agr. Food Chem. 23: 677 (1975).

10. Woolson, E. A., and Kearney, P. C. Persistence and reactions of ^{14}C-cacodylic acid in soils. Environ. Sci. Technol. 7: 47 (1973).

11. Ferguson, J. F., and Gavis, J. A review of the arsenic cycle in natural waters. Water Res. 6: 1259 (1972).

12. Klein, D. H. Fluxes, residence times, and sources of some elements to Lake Michigan. Water, Air Soil Pol. 4: 3 (1975).

13. Seydel, I. S. Distribution and circulation of arsenic through water, organisms and sediments of Lake Michigan. Arch. Hydrobiol. 71: 17 (1972).

14. Wilder, H. B. Investigation of the occurrence and transport of arsenic in the Upper Sugar Creek watershed, Charlotte, N. C. Geol. Survey Prof. Paper 800-D, D205 (1972).

15. Sugawara, K., and Kanamori, S. Spectrophotometric determination of trace amounts of arsenate and arsenite in natural waters with special reference on the phosphate determination. Bull. Chem. Soc. Japan. 37: 1358 (1964).

16. Braman, R. S. Arsenic in the environment. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

17. Johnson, D. L. Bacterial reduction of arsenate in sea water. Nature 240: 44 (1972).

18. Isensee, A. R., et al. Distribution of alkyl arsenicals in model ecosystem. Environ. Sci. Technol. 7: 841 (1973).

19. Schuth, C. K., et al. Distribution of ^{14}C and arsenic derived from [^{14}C]-Cacodylic acid in an aquatic ecosystem. J. Agr. Food Chem. 22: 999 (1974).

20. Woolson, E. A., Isensee, A. R., and Kearney, P. C. Distribution and isolation of radioactivity from ^{74}As-arsenate and ^{14}C-methanearsonic acid in an aquatic model ecosystem. Pestic. Biochem. Physiol. 6: 261 (1976).

21. Woolson, E. A. Bioaccumulation of arsenicals. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

22. Vinogradov, A. P. The elementary chemical composition of marine organisms. In: Sears Foundation for Marine Research. Memoir II, Yale University, New Haven, Conn., 1953.

23. Carey, A. E., et al. Organochlorine pesticide residues in soils and corps of the corn belt region, United States—1970. Pestic. Monit. J. 6: 369 (1973).

24. Wiersma, G. B., Tai, H., and Sand, P. F. Pesticide residue levels in soils, FY 1969—National Soils Monitoring Program. Pestic. Monit. J. 6: 194 (1972).

25. Durum, W. H., Hem, J. D., and Heidel, S. G. Reconnaissance of Selected Minor Elements in Surface Waters of the United States. Geological Survey Circular 643, USDI, Wash., D. C., 1971.

26. McCabe, L. J., et al. Survey of community water supply systems. J. Am. Water Works Assoc. 62: 670 (1970).

27. Crecelius, E. A., Bothner, M. H., and Carpenter, R.

Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9: 325 (1975).

28. Parker, R. L. Composition of the earth's crust. Data of Geochemistry, 6th ed. Michael Fleischer, Ed., In: Geological Survey Prof. Paper, 440-D (1967).

29. Ruch, R. R., Kennedy. E. J., and Shimp, N. F. Lake Michigan bottom sediments. IV. Distribution of arsenic in Unconsolidated sediments from southern Lake Michigan. Environ. Geol. Notes No. 37: 16 pp. (1970).

30. Cox, D. P., and Alexander, M. Production of trimethylarsine gas for various arsenic compounds by three sewage fungi. Bull. Environ. Contam. Toxicol. 9: 84 (1973).

31. McBride, B. C., and Wolfe, R. S. Biosynthesis of dimethylarsine by *Methanobacterium*. Biochem. 10: 4312 (1971).

32. Challenger, F., Lisle, D. B., and Dransfield, P. B. Biological methylation. XIV. The formation of trimethylarsine and dimethyl selenide in mold cultures from methyl sources containing carbon^{14}. J. Chem. Soc. 1954: 1760.

33. Lasko, J. U., and Peoples. S. A. Methylation of inorganic arsenic by mammals. J. Agr. Food Chem. 23: 374 (1975).

34. Peoples, S. A. Review of arsenical pesticides. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

35. Johnson, D. L., and Braman, R. S. Alkyl- and inorganic arsenic in air samples. Chemosphere 6: 333 (1975).

36. Crecelius, E. A., and Carpenter, R. Arsenic distribution in waters and sediments of the Puget Sound region. Paper presented at first Ann. NSF Trace Contaminants Conf., Oak Ridge Natl. Lab., Oak Ridge, Tenn., Aug. 8–10, 1973.

37. Carton, R. Technical and Microeconomic Analysis of Arsenic and Its Compounds. EPA 560/6-76-016, Office of Toxic Substances. Washington, D. C. (1976).

38. Sullivan, R. J. Preliminary Air Pollution Survey of Arsenic and Its Compounds, a Literature Review. Natl. Air Poll. Control Adm. No. APTD 69-26. 60 pp (1969).

39. Lunde, G. The absorption and metabolism of arsenic in fish. Fiskeridiv. (Norway) SKR, Teknol. Unders. 5: 16 (1972).

40. Lunde, G. Separation and analysis of organic-bound and inorganic arsenic in marine organisms. J. Sci. Food Agric. 24: 1021 (1973).

41. Lunde, G. The synthesis of fat and water soluble arseno organic compounds in marine and limnetic algae. Acta Chem. Scand. 27: 1586 (1973).

42. Challenger, F., Higginbottom, C., and Ellis, L. Formation of organometalloidal compounds by microorganisms. J. Chem. Soc. 1933, 95.

43. Thom, C., and Raper, K. B. The arsenic fungi of GOSIO. Science 76: 548 (1932).

44. Zussman, R. A., Vicher, E. E. and Lyon, I. Arsine production by *Trichophyton rubrum*. J. Bacteriol. 81: 157 (1961).

45. Merrill, W., and French, D. W. The production of arsenous gases by wood-rotting fungi. Proc. Minn. Acad. Sci. 31: 105 (1964).

46. Epps, E. A., and Sturgis, M. B. Arsenic compounds toxic to rice. Soil Sci. Soc. Am. Proc. 4: 215 (1939).

47. Cox, D. P. Microbiological methylation of arsenic. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

48. Braman, R. S., and Foreback, C. C. Methylated forms of arsenic in the environment. Science 182: 1247 (1973).

49. Von Endt, D. W., Kearney, P. C., and Kaufman, D. D. Degradation of MSMA by soil microorganisms. J. Agr. Food Chem. 16: 17 (1968).

50. Sandberg, G. R., and Allen, I. K. A Proposed arsenic cycle in an agronomic ecosystem. In: Arsenical Pesticides (ACS Symp. Ser. 7). E. A. Woolson, Ed., American Chemical Society, Washington, D. C., 1975.

51. Tammes, P. M., and de Lint, M. M. Leaching of arsenic from soil. Neth. J. Agr. Sci. 17: 128 (1969).
52. Steevens, D. R., Walsh, L. M., and Keeney, D. R. Arsenic residues in soil and potatoes from Wisconsin potato fields. Pestic. Monit. J. 6: 89 (1972).
53. Sandberg, G. R., Allen, I. K., and Dietz, E. A., Jr. Arsenic residues in soils treated with six annual applications of MSMA and cacodylic acid (CA). Progress Report 73 Wes

8-9-10, Ansul Co., Weslaco, Texas, 1973.
54. Hiltbold, A. E., Hajek, B. F., and Buchanan, G. A. Distribution of arsenic in soil profiles after repeated applications of MSMA. Weed Sci. 22: 272 (1974).
55. Woolson, E. A., Axley, J. H., and Kearney, P. C. The chemistry and phytotoxicity of arsenic in soils: I. Contaminated field soils. Soil Sci. Soc. Amer. Proc. 35: 938 (1971).